

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 March 2002 (07.03.2002)

PCT

(10) International Publication Number
WO 02/18486 A2

- (51) International Patent Classification: C08L 1/00
- (21) International Application Number: PCT/US01/25821
- (22) International Filing Date: 20 August 2001 (20.08.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
09/645,320 25 August 2000 (25.08.2000) US
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- (84) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— without international search report and to be republished upon receipt of that report
- For neo-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/18486 A2

(54) Title: HYDROPHILIC INSOLUBLE CELLULOSE AS RHEOLOGICAL MODIFIER IN WATER-IMMISCIBLE LIQUIDS

(57) Abstract: Hydrophilic insoluble cellulose acts as a rheological modifier in water-immiscible liquids when mixed with co-agents capable of forming hydrogen bonds with the hydroxyl groups on the surface of the cellulose fiber and which are soluble in the water-immiscible liquid. The co-agents of the invention may be surfactants or polymers, and are added to the water-immiscible liquid either prior to or during mixing with the hydrophilic insoluble cellulose. Multiple co-agents can be added to the cellulose during or after addition to the water-immiscible liquid. The composition generally has a weight ratio of co-agent to cellulose of 1:4 to 30:1.

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TITLE

HYDROPHILIC INSOLUBLE CELLULOSE AS
RHEOLOGICAL MODIFIER IN WATER-IMMISCIBLE LIQUIDS

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FIELD OF THE INVENTION

The present invention relates to a composition comprising
10 hydrophilic insoluble cellulose and certain co-agents,
wherein the composition acts as a rheological modifier in
water-immiscible liquids. The invention also relates to
a process for making the composition and for making the
resulting rheologically modified dispersion. The co-
15 agent(s) used in the invention is capable of forming
hydrogen bonds with the hydroxyl groups on the surface of
the cellulose fiber and is soluble in the water-
immiscible liquid. The hydrophilic insoluble cellulose
can be produced by bacteria or by chemical and/or
20 mechanical modification of low surface area cellulose
derived from cotton, wood pulp, oat fiber, cereal

cellulose, corn cellulose, sugar beet and other plant cellulose well-known to one skilled in the art.

BACKGROUND OF THE INVENTION

5

Rheological modifiers of water-immiscible liquids, which include the category of oil thickeners, have long been sought for a number of industrial applications, including use in oil drilling fluids, paint solvents, solvent-born
10 or solvent-free epoxy systems, industrial lubricants and grease, thin film and powder coatings and vegetable oils. Rheological modifiers have the ability to form stable, highly viscous fluids on suspension in water-immiscible liquids.

15

It is important that a rheological modifier impart a pseudoplastic character to the liquid that allows for rapid decrease in viscosity under applied shear. It is also important that a rheological modifier be capable of
20 maintaining viscosity and yield stress in pure-oil systems. In addition, it would be advantageous for a rheological modifier to have efficacy at small concentrations, to maintain the integrity of the water-immiscible system which may further potentially provide economic cost-savings benefits. It would also be
25 advantageous for a rheological modifier to be able to maintain viscosity and yield stress under a range of temperature conditions and to provide long-term suspension for an extended shelf-life.

30

The use of polymers as viscosifiers in water-immiscible

liquids is well-known in the art. For example, U.S. Patent No. 4,670,501 and U.S. Patent No. 4,777,200 disclose polymeric viscosifiers having a dry weight particle size below 10 μm that are insoluble in water-
5 immiscible liquid but can be swollen by absorbing surrounding water found in the liquid. The polymeric viscosifiers are added as co-agents to the water-immiscible liquid to provide the desired viscosity. The polymeric viscosifiers of these systems have limitations
10 however, in that they require the presence of water and thus cannot function in pure oil systems, and also have limited pseudoplasticity.

The use of cellulose to viscosify liquids is also known
15 in the art, but has not been known for use in water-immiscible liquids. U.S. Patent No. 5,366,750 discloses the addition of high surface area cellulose to edible liquids, but such use was generally confined to hydrophilic liquids. Similarly, U.S. Patent No.
20 5,487,419 and U.S. Patent No. 4,481,076, which both disclose the suspension of microdenominated or microfibrinous cellulose with carbohydrate co-agents in water-based or polar solvents, also confines the use of cellulose to hydrophilic liquids.

25

It would be highly desirable to obtain a composition that is able to rheologically modify water-immiscible liquids without the required presence of water or hydrophilic liquids. It would also be highly desirable if this
30 composition could provide long term suspension of colloids and particles for an extended shelf-life,

- increased viscosity and yield stress, stability under a range of temperature conditions, highly pseudoplastic character under applied shear and improved efficacy at small concentrations. Co-agents which can be used in the composition to stabilize the rheologically-modified water-immiscible liquids would also be highly desirable.

SUMMARY OF THE INVENTION

- This invention relates to a composition comprising hydrophilic insoluble cellulose and a co-agent capable of forming hydrogen bonds with said hydrophilic insoluble cellulose, wherein said co-agent is soluble in a water-immiscible liquid. This invention is also directed to a process for making the composition.

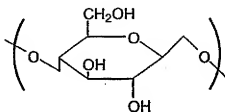
- This invention is further directed to a water-immiscible liquid that is rheologically modified by the composition described above, and to applications for the rheologically-modified water-immiscible liquid, such as oil drilling fluids, paint solvents, solvent-born or solvent-free epoxy systems, industrial lubricants and grease, thin film and powder coatings and vegetable oils.

DETAILED DESCRIPTION OF THE INVENTION

- It has recently been discovered that hydrophilic insoluble cellulose, such as bacterial cellulose, can serve as rheological modifiers for water-immiscible liquids. The hydroxyl groups on the surface of the cellulose fibers can be stabilized in water-immiscible

liquids by association with certain co-agents through hydrogen bonding. The resultant solutions have enhanced rheological properties, such as long term suspension stability of colloids and particles for an extended shelf-life, improved stability under a range of temperature conditions, highly pseudoplastic character under applied shear, improved efficacy at small concentrations and most significantly, functionality without the required presence of water or a hydrophilic liquid.

Cellulose is a linear polymer of D-glucose in which the sugar residues are connected by $\beta(1,4)$ linkages, as represented below:



The term "hydrophilic insoluble cellulose" refers to cellulose which has an affinity to water but has a solubility of less than about 100 mg per liter in both water and water-immiscible systems. Preferably, the cellulose of this invention is a high surface area cellulose. High surface area cellulose can be produced by bacteria or by chemical and/or mechanical modification of low surface area cellulose such as cotton, wood pulp, oat fiber, cereal cellulose, corn cellulose, sugar beet

and other plant cellulose well-known to one skilled in the art.

Bacterially produced cellulose, because of its source and
5 recovery conditions, has a high surface area that together with certain co-agents can form a well dispersed cellulose network in water-immiscible liquids. This results in a substantial increase in the viscosity of the water-immiscible system and usually in measurable yield
10 stress that must be overcome before a sample will flow.

The surface area of most plant derived cellulose is substantially less than the surface area of bacterially produced cellulose. Because of this, plant derived
15 cellulose materials do not appreciably viscosify aqueous systems unless their surface area is increased. The surface area of plant-derived cellulose may be increased by acid digestion and/or homogenization or extension homogenization at high pressures.

20 Most preferably, the cellulose of this invention is high surface area cellulose produced from bacteria. Bacterially produced cellulose may be obtained directly by bacterial fermentation of *Acetobacter xylinum*.
25 Cellulose fibers obtained by microbial fermentation of *Acetobacter xylinum* have an average diameter of about 0.1 μm and an average length of about 10 to about 15 μm . In comparison, conventional plant cellulose has an average diameter of about 30 μm and an average length of
30 about 300 μm . Consequently, cellulose obtained by bacterial fermentation has up to 200 times more surface

area than an equivalent amount of plant derived cellulose. A process for obtaining cellulose by bacterial fermentation from *Acetobacter* strains is described in U.S. Patent No. 5,079,162 and U.S. Patent

5 No. 5,144,021, the entire contents of which are incorporated by reference herein. Wet cake cellulose, containing approximately 80 to about 90 wt% water can be produced using the methods and conditions disclosed in the above-mentioned patents. Alternative methods of

10 obtaining bacterial cellulose are well-known in the art.

Both plant-derived cellulose and bacterial cellulose are associated with flocculation problems in non-aqueous solutions, whereby the cellulose fibers have a pronounced

15 tendency to self associate into larger, less efficient bundles. The high surface area cellulose cannot interact with the water-immiscible liquid to disperse evenly and thus quickly separates from solution.

20 Dispersing co-agents may be used in conjunction with cellulose to inhibit the cellulose-to-cellulose interaction and thus enhance the ability of individual fibers to interact with the water-immiscible liquid. It is believed that the co-agent interacts with the hydroxyl

25 groups on the glucose moieties by hydrogen bonding, resulting in the formation of cellulose fiber having a hydrophobic surface, which in turn allows for improved dispersion and stabilization of the cellulose/co-agent composition in the water-immiscible liquid.

30

As used herein, the term "water-immiscible liquid" refers

to any non-aqueous or hydrophobic solvent which separates from solution into two distinct phases when mixed with water. The water-immiscible liquid may be, for example, a chlorinated hydrocarbon, but is generally non-polar and is preferably a mineral oil, vegetable oil, refined kerosene, diesel oil, paraffin oil, white spirit or aviation crude oil, oil of an oil-based paint, grease, solvent-borne or solvent-free epoxy systems, thin film and powder coating, or other water-immiscible liquids well known in the art.

In the present invention, co-agents are commonly added to cellulose prior to and during activation in the water-immiscible liquid to reduce the formation of inter-cellulose associations during the activation process. High shear dispersion, or "activation" is used to thoroughly mix the cellulose and co-agent in a solvent to increase the cellulose surface area and to form a smooth, uniform dispersion. Activation is typically accomplished by a homogenizer, but in some instances, as in the case of bacterial cellulose, a high shear mixer is adequate. The term "activated" describes a process in which the 3-dimensional structure of cellulose is dispersed in the solvent such that the cellulose imparts to the fluid composition such properties as thickening, increased yield stress, heat stability, suspension properties, freeze-thaw stability, flow control, foam stabilization, coating and film formation, and the like. The activation "teases apart" the cellulose fibers to expand the cellulose to create a network of highly intermeshed fibers with a very high surface area. The expanded

cellulose, formed by activation, significantly modifies the properties of the base solvent or composition, thereby "activating" it.

- 5 In order to function effectively as dispersing co-agents, the co-agents of the present invention must (a) be capable of forming hydrogen bonds with the hydrophilic insoluble cellulose, and (b) be soluble in water-immiscible liquid. In a preferred embodiment of the
- 10 invention, the co-agents are surfactants, such as long-chain fatty acids, fatty acid derivatives, mono- and diglycerides, alkylamines and alcohols. In a particularly preferred embodiment, the co-agents are long chain alkylamines, or mixtures of long-chain alkylamines.
- 15 Preferably, the alkylamines are long chain amines comprising four to thirty carbons. Most preferably, the long chain amine comprises eight to eighteen carbons. The most preferred surfactant co-agents of this invention are dodecylamine or mono- or di- glycerides.

20

- In another preferred embodiment, the co-agents are polymers, such as alkylated polyvinylpyrrolidones that are graft copolymers prepared from α -olefins, e.g., polyvinylpyrrolidone-graft-hexadecene (PVPGH) or 1-
- 25 ethenylhexadecyl or eicosene or tricontanyl, which are sold commercially as GANEX[®] polymers by ISP Corporation in Wayne, NJ. The polymers tend to be high molecular weight compounds which disperse less easily than surfactants. Preferably, if only polymers are acting as co-agents and
- 30 no surfactant co-agents are present, the polymer is a homopolymer such as polyvinyl pyrrolidone or any other

suitable homopolymer well-known in the art.

Preferably, particularly for high temperature applications, both surfactants and polymers are present

- 5 as co-agents in the invention. When both surfactants and polymers are present as co-agents, both must be charge-compatible, meaning that they must either be both anionic, both cationic, or one may be neutral.

- 10 Generally, the weight ratio of co-agent, or mixture of co-agents, to cellulose ranges from 1:4 to 30:1, and is most preferably 1:2 to 10:1. Increasing the temperature increases the dispersability of the co-agents and cellulose in the solvent. In addition, because only
- 15 small quantities of the co-agents are required in this invention, the solubility of the co-agents in the water-immiscible liquid need not be high. Preferably, the co-agents of the invention have a solubility of at least 500 mg per liter in the water-immiscible liquid.

- 20 In a preferred embodiment, activation of the cellulose with the co-agent first takes place in a water-miscible solvent. Once activated in a water-miscible solvent, the cellulose/co-agent composition can then be added to the
- 25 water-immiscible liquid and re-dispersed, or re-activated, by high shear mixing or homogenization. In a preferred embodiment, the cellulose/co-agent composition may be tray dried, drum dried or dried by any method well known in the art, prior to re-dispersion in the water-
- 30 immiscible liquid.

Preferably, at least one co-agent is present prior to or during activation of the cellulose in the water-miscible solvent to form compositions having superior stability and viscosity. The co-agents may be in any form, as

5 solid or liquid, when mixed with the cellulose. If more than one co-agent is used, each additional co-agent may be added to the cellulose either as a mixture with other co-agents or separately, and in any order, either prior to, simultaneously with, or subsequent to dispersion of

10 the cellulose material in the water-miscible solvent.

Preparation of a Hydrophilic Insoluble Cellulose Slurry

15 Preparation of the hydrophilic insoluble cellulose slurry involves mixing the cellulose, and possibly a co-agent, in a water-miscible solvent. Preferably, the cellulose is already in wet cake form containing about 10 to about 20% cellulose and about 80 to about 90% water. The

20 resulting dispersion of wet cake cellulose in water-miscible solvent will generally contain about 0.1 to about 6 wt% cellulose, preferably about 0.5 to about 3 wt% cellulose.

25 Most preferably, water is used as the water-miscible solvent, but other organic solvents may also be used, provided that they are water-miscible. Exemplary water-miscible solvents useful for dispersing cellulose include ethanol, propanol, isobutanol, isopropanol, methyl or

30 dimethyl sulfoxide, butanol and mixtures thereof or with water. In one preferred embodiment, the water-miscible

solvent is isopropanol or a constant boiling mixture of isopropanol and water. The dispersion contains the water-miscible solvent in an amount from about 50 to about 99 wt%, and preferably in an amount from about 65 to about 97 wt% of the total dispersion.

The hydrophilic insoluble cellulose slurry is prepared by mixing the cellulose, the water-miscible solvent and possibly a co-agent, in either a homogenizer, such as an APV Homogenizer® (APV Limited, West Sussex, U.K.); in a high shear mixer or in both. In a most preferred embodiment, the cellulose, co-agent and water-miscible solvent are first mixed in a high shear mixer prior to mixing in a homogenizer.

15

Addition of Co-Agents to Hydrophilic Insoluble Cellulose

As discussed above, the cellulose may be mixed with a co-agent in the water miscible solvent by homogenization, high shear mixing or both. In a preferred embodiment, the cellulose and the co-agent preferably combine to make a total weight of about 0.3 wt% to about 50 wt% in the water-miscible solvent, most preferably about 1 wt% to about 30 wt% of the dispersion. While the cellulose is added at a range of 0.1 wt% to about 6 wt%, the co-agent is added at about 0.2 wt% to about 44 wt% of the dispersion.

As previously noted, any of a variety of co-agents may be used in combination with the cellulose, as may be required for a specific application. Preferably, in

high temperature applications, both surfactants and polymers are present as co-agents. Most preferably, in high temperature applications, the surfactant is dodecylamine or mono- or di-glyceride, and the polymer is

5 PVPGH or polyvinyl pyrrolidone tricontene (PVPT).

If the co-agent is a surfactant or is a plurality of surfactants, then preferably at least one surfactant is added prior to or during activation of the cellulose in

10 the water-miscible solvent. In contrast, if no surfactants are added and only polymers are to be added, then the polymer should be a homopolymer and the solvent should be a less polar water-miscible solvent, such as isopropanol or isobutanol or others well-known in the

15 art. Alternatively, in another preferred embodiment, polymer co-agents are not added to the water-miscible solvent at all, but are added with the cellulose prior to or during re-activation in the water-immiscible liquid.

20 Where both surfactants and polymers are present as co-agents, then preferably at least one surfactant co-agent is added prior to or during activation of the cellulose in the water-miscible solvent. The remaining surfactants may be added at any time subsequent to activation in the

25 water-miscible solvent, and the polymer or polymers are preferably added directly to the water-immiscible liquid prior to or during activation.

Activation of the cellulose, and any possible co-agents,

30 in the water-miscible solvent may be accomplished by a high shear mixing device or a pressure-drop homogenizer

- or both, as described above. Preferably, the composition is first mixed in a high shear mixer before being passed through a pressure-drop homogenizer at approximately 8,000 psi for multiple passes, depending on the source of the cellulose and the desired viscosity. The compositions will typically exhibit an increase in viscosity with each successive pass through the homogenizer. For high surface area cellulose produced from bacteria, typically only one or two passes is required. For high surface area cellulose produced from plants, up to fifty passes may be desired. The surface area and viscosity of the cellulose may be adjusted by using methods well-known to one skilled in the art, e.g., adjusting the homogenization pressure as well as the total number of passes through the homogenizer or high shear mixer. When using a pressure-drop homogenizer, the pressure may be increased to as high as 26,000 psi. As noted above, for high surface area cellulose produced by bacteria, a high shear mixer may alone be sufficient. In one preferred embodiment, the cellulose/co-agent composition may be heated to between about 30°C to about 100°C prior to activation, as required to melt the co-agent and/or aid in dispersion.
- After activation in the water-miscible solvent, the resulting slurry can then be transferred directly into the water-immiscible liquid for re-dispersion. Alternatively, the resulting slurry can first be tray dried or drum dried at a temperature below the vaporization point of any added co-agents, generally at temperatures ranging from about 35°C to about 150°C. If

dried, the resulting slurry can be milled to a mesh size ranging from about 1.7 mm (about 10 mesh size) to about 0.15 mm (about 200 mesh size) and stored for later re-dispersion in the water-immiscible liquid. The dried
5 form of the resulting cellulose or cellulose/co-agent composition is preferable for storage and ease of transport.

Preparation of Hydrophilic Insoluble Cellulose
10 In Water-Immiscible Liquid

The resulting slurry prepared above is then re-dispersed, preferably with polymer co-agents, in a water-immiscible liquid to produce suspensions or dispersions possessing
15 excellent viscosity and yield stress. In the instance where only a polymer is added as co-agent, this may be the first time the co-agent is introduced. The quantity of co-agent or the types of co-agents used in combination with the re-dispersible cellulose will also vary as
20 required for a specific application. Generally, the amount of co-agent or co-agents present in the final water-immiscible dispersion is about 0.1 to about 3 wt% of the total weight of the dispersion. The amount of cellulose present in the final water-immiscible
25 dispersion is generally an amount of about 0.05 to about 5 wt%, and preferably about 0.1 to about 1.5 wt% of the total weight of the dispersion.

Preferably, where both surfactants and polymers are
30 present as co-agents, the polymers may be added to the water-immiscible liquid with the cellulose/surfactant

slurry for re-dispersion. The activation of the cellulose/surfactant slurry, plus added polymer, in the water-immiscible liquid is accomplished in the same manner as the dispersion in water-miscible solvent described above. The cellulose/surfactant/polymer composition is activated by mixing in a homogenizer, high shear mixer, or both to attain the desired surface area and viscosity using methods well-known to one skilled in the art. In the instance where the cellulose is produced by high surface area bacteria, activation in a high shear mixer may alone be sufficient.

The examples which follow are intended as an illustration of certain preferred embodiments of the invention, and no limitation of the invention is implied.

Example 1

Cellulose/Dodecylamine Composition as Rheological Modifier in Mineral Oil

A slurry of hydrophilic insoluble cellulose was prepared by mixing 573.2 g cellulose wet cake fiber (90.0 g cellulose fiber and 483.2 g water) with 180.00 g (6.0 wt%) of the surfactant dodecylamine and 2246.8 g water in a high shear mixer for about 10 minutes at 2,000 rpm. The dispersion was then passed through an APV Homogenizer® (APV Limited, West Sussex, U.K.) for 15 minutes at 8,000 psi for two passes. The resulting slurry, containing approximately 3 wt% cellulose, was tray dried at 50 °C and milled to about 1.7 mm (approximately 10 mesh size).

- 1.69 g of the milled cellulose/dodecylamine composition was then re-dispersed in 170 g mineral oil by high shear mixing in a Waring Blender® (from Dynamics Corp. of America, New Hartford, CN) for 5 minutes to provide a dispersion containing about 0.33 wt% cellulose and about 0.66 wt% dodecylamine. Samples of the resulting oil and cellulose/dodecylamine composition were hot rolled in a temperature controlled roller oven for approximately 19 hours at about 300°F (150°C) and about 200 psi (14 kg/cm²) of nitrogen gas. In addition, another sample of the mineral oil was stored at room temperature for over one and a half years.

- The mineral oil modified by the above cellulose/dodecylamine composition showed an appreciable increase in viscosity, both before and after hot-rolling, when compared to base mineral oil alone. The mineral oil sample which was stored over 1½ years showed no visible separation of oil and cellulose, while viscosity increased slightly.

The viscosities of the above mineral oil compositions are shown in Table 1 below.

Table 1: Viscosity of Mineral Oil Rheologically Modified
by Cellulose/Dodecylamine Composition

Composition	Shear Rate (s^{-1})				
	5.1	10.2	51	170	340
Base Mineral Oil	—	—	—	42 cP	46 cP
Modified Mineral Oil (Before hot rolling)	800 cP	625 cP	285 cP	165 cP	126 cP
Modified Mineral Oil (After hot rolling)	700 cP	500 cP	220 cP	130 cP	104.25 cP
Modified Mineral Oil (After 1½ Years)	1200 cP	750 cP	305 cP	183 cP	130.5 cP

Example 2

Cellulose/Dodecylamine/PVPGH Combination
As Rheological Modifier in Mineral Oil

1.69 g of the milled cellulose/dodecylamine composition prepared in Example 1, plus 1.12 g of the polymer poly(vinyl pyrrolidinone) graft hexadecene (PVPGH), were

dispersed in 170 g mineral oil by high shear mixing in a Waring Blender® (from Dynamics Corp. of America, New Hartford, CN) for 5 minutes. The resulting dispersion contained about 0.33 wt% cellulose, about 0.66 wt% dodecylamine and about 0.66 wt% PVPGH.

Samples of the resulting oil modified by the cellulose/dodecylamine/PVPGH combination were hot rolled in a temperature controlled roller oven for approximately 10 19 hours at about 300°F (150°C) and about 200 psi (14 kg/cm²) of nitrogen gas.

The mineral oil modified by the cellulose/dodecylamine/PVPGH combination showed an 15 appreciable increase in viscosity, both before and after hot-rolling, when compared to base mineral oil alone. The viscosities of the mineral oil compositions, both modified and unmodified, before and after hot rolling, are shown in Table 2 below.

20

Table 2: Viscosity of Mineral Oil Rheologically Modified
by Cellulose/Dodecylamine/PVPGH Combination

Composition	Shear Rate (s^{-1})				
	5.1	10.2	51	170	340
Base Mineral Oil	—	—	42 cP	46 cP	
Modified Mineral Oil (Before hot rolling)	—	725 cP	275 cP	162 cP	124 cP
Modified Mineral Oil (After hot rolling)	600 cP	425 cP	220 cP	144 cP	132 cP

Example 3

Cellulose/Dodecylamine/PVPT Combination As Rheological Modifier in Mineral Oil

1.5 g of the milled cellulose/dodecylamine composition prepared in Example 1, plus 0.5 g of the polymer polyvinyl pyrrolidone tricontene (PVPT) were dispersed in 150 g of mineral oil by high shear mixing in a Waring Blender® (from Dynamics Corp. of America, New Hartford, CN) for 5 minutes. The resulting dispersion contained about 0.25 wt% cellulose, about 0.5 wt% dodecylamine and about 0.5 wt% PVPT.

The mineral oil modified by the cellulose/dodecylamine/PVPT combination showed a significant increase in viscosity when compared to base mineral oil alone or to the mineral oil dispersions

- 5 modified by cellulose/dodecylamine or cellulose/dodecylamine/PVPGH. The viscosities of the mineral oil compositions, both modified and unmodified, are shown in Table 3 below.

10 Table 3: Viscosity of Mineral Oil Rheologically Modified by Cellulose/Dodecylamine/PVPT Combination

Composition	Shear Rate (s^{-1})				
	5.1	10.2	51	170	340
15 Base Mineral Oil	—	—	66 cP	62 cP	
Modified Mineral Oil	4500 cP	2850 cP	930 cP	462 cP	306 cP

20

Example 4

Cellulose/Dodecylamine Composition
As Rheological Modifier in Canola Oil

25

- 2.25 g of the milled cellulose/dodecylamine composition prepared in Example 1 was then re-dispersed in 300 g of canola oil by high shear mixing in a Waring Blender® (from Dynamics Corp. of America, New Hartford, CN) for 5 minutes to provide a dispersion containing about 0.25 wt% cellulose, about 0.5 wt% dodecylamine.
- 30

The modified canola oil showed a marked increase in yield stress, as measured by the Bohlin stress rheometer. The modified canola oil revealed a yield stress of 7.067 Pa, as compared to a base canola oil yield stress of 0 Pa.

5

In addition, the canola oil modified by the cellulose/dodecylamine composition showed a significant increase in viscosity when compared to base canola oil alone. The viscosities of the canola oil compositions, both modified and unmodified, are shown in Table 4 below.

10

Table 4: Viscosity of Canola Oil Rheologically Modified by Cellulose/Dodecylamine Composition

15

Composition	Shear Rate (s^{-1})				
	5.1	10.2	51	170	340
Base Canola Oil	—	—	—	60 cP	60 cP
Modified Canola Oil	3450 cP	2175 cP	600 cP	363 cP	315 cP

20

Example 5

25

Cellulose/Monoglyceride Composition as Rheological Modifier in Canola Oil

A slurry of hydrophilic insoluble cellulose was prepared by mixing 32 g cellulose wet cake fiber (5.0 g cellulose fiber and 27.0 g water) with 10.0 g (3.85 wt%) of the surfactant monoglyceride (myvatex 3-50® from Quest International, Hoffman Estates, IL) and 218.0 g water in a high shear mixer for about 10 minutes at 2,000 rpm.

30

The resulting slurry, containing approximately 1.92 wt% cellulose, was tray dried at 50 °C and milled to about 1.7 mm (approximately 10 mesh size).

- 5 2.25 g of the milled cellulose/monoglyceride prepared in Example 5 was re-dispersed in 300 g of canola oil by high shear mixing in Waring Blender® for 5 minutes to provide a dispersion containing 0.25% cellulose and 0.5 wt% monoglyceride.

10

The canola oil modified by the cellulose/monoglyceride composition showed an appreciable increase in viscosity, when compared to base canola oil alone. The viscosities of the canola oil compositions, both modified and

- 15 unmodified, are shown in Table 5 below.

Table 5: Viscosities of Canola Oil Rheologically
Modified by Cellulose/Monoglyceride Composition

Composition	Shear Rate (s^{-1})				
	5.1	10.2	51	170	340
Base Canola Oil	—	—	—	60 cP	60 cP
Modified Canola Oil	600 cP	440 cP	250 cP	174 cP	145.5 cP

Example 6

Cellulose/Monoglyceride Composition as
Rheological Modifier in Paraffin Oil

2.25 g of the milled cellulose/monoglyceride composition prepared in Example 5 was re-dispersed in 300 g paraffin oil by high shear mixing in a Waring Blender® (from Dynamics Corp. of America, New Hartford, CN) for 5 minutes to provide a dispersion containing about 0.25 wt% cellulose and about 0.5 wt% monoglyceride.

The paraffin oil modified by the cellulose/monoglyceride composition showed an appreciable increase in viscosity. The viscosity of the paraffin oil composition is shown in Table 6 below.

Table 6: Viscosity of Paraffin Oil Rheologically
Modified by Cellulose/Monoglyceride Composition

Composition	Shear Rate (s^{-1})				
	5.1	10.2	51	170	340
Base Paraffin Oil	—	—	—	26 cP	26 cP
Modified Paraffin Oil	550 cP	350 cP	155 cP	100 cP	84 cP

Other variations and modifications of this invention will
be obvious to those skilled in the art. This invention
is not limited except as set forth in the art.

WHAT IS CLAIMED IS:

1. A composition comprising:
 - (a) hydrophilic insoluble cellulose; and,
 - (b) a co-agent capable of forming hydrogen bonds with said hydrophilic insoluble cellulose, wherein said co-agent is soluble in a water-immiscible liquid.
2. The composition of claim 1, wherein the hydrophilic insoluble cellulose is high surface area cellulose.
3. The composition of claim 2, wherein the high surface area cellulose is produced from bacteria.
4. The composition of claim 2, wherein the high surface area cellulose is derived from low surface area plant cellulose.
5. The composition of claim 4, wherein the plant cellulose is selected from the group consisting of cotton, wood pulp, oat fiber, cereal cellulose, corn cellulose, sugar beet.
6. The composition of claim 1, wherein the co-agent is a surfactant.
7. The composition of claim 6, wherein the co-agent is selected from the group consisting of long-chain fatty acids, fatty acid derivatives, mono- and di-glycerides, alkylamines and alcohols.

8. The composition of claim 7, wherein the surfactant is a long chain alkylamine or a mixture of long chain alkylamines.

9. The composition of claim 8, wherein the alkylamine comprises four to thirty carbons.

10. The composition of claim 9, wherein the alkylamine is dodecylamine.

11. The composition of claim 7, wherein the surfactant is monoglyceride.

12. The composition of claim 1, wherein the co-agent is a polymer.

13. The composition of claim 12, wherein the polymer is an alkylated polyvinylpyrrolidone.

14. The composition of claim 13, wherein the polymer is polyvinylpyrrolidone graft hexadecene.

15. The composition of claim 13, wherein the polymer is polyvinylpyrrolidone tricontene.

16. The composition of claim 1, wherein a weight ratio of co-agent or a mixture of co-agents to cellulose ranges from about 1:4 to about 30:1.

17. The composition of claim 16, wherein the weight ratio of co-agent or the mixture of co-agents to

cellulose ranges from about 1:2 to about 10:1.

18. The composition of claim 1, further comprising multiple co-agents.

19. The composition of claim 18, wherein the multiple co-agents include both surfactants and polymers.

20. The composition of claim 19, wherein the surfactants and polymers are charge compatible.

21. A rheologically modified water-immiscible liquid comprising a rheologically modifying effective amount of the composition of claim 1 and a water-immiscible liquid.

22. The water-immiscible liquid of claim 21, wherein the water-immiscible liquid is selected from the group consisting of mineral oil, vegetable oil, or other refined kerosene, diesel oil, paraffin oil, white spirit or aviation crude oil, oil of an oil-based paint, grease, solvent-born or solvent-free epoxy systems, or thin film and powder coating.

23. A process for making a rheologically modifying composition for a water-immiscible liquid comprising the step of mixing hydrophilic insoluble cellulose with a co-agent, wherein said co-agent is capable of forming hydrogen bonds with said hydrophilic insoluble cellulose and is soluble in said water-immiscible liquid.

24. The process of claim 23, wherein mixing of the cellulose and co-agent is first accomplished by high

shear mixing.

25. The process of claim 23, wherein mixing of the cellulose and co-agent is accomplished by a homogenizer.

26. The process of claim 23, wherein mixing of the cellulose and co-agent is accomplished in a water-miscible solvent.

27. The process of claim 26, wherein the water-miscible solvent is selected from the group consisting of ethanol, propanol, isobutanol, isopropanol, methyl sulfoxide, dimethyl sulfoxide, butanol, water and mixtures thereof.

28. The process of claim 26, wherein the co-agent is a surfactant.

29. The process of claim 28, wherein the surfactant is selected from the group consisting of long-chain fatty acids, mono- and di- glyceride, alkylamines, and long chain alcohols.

30. The process of claim 29, further comprising the step of adding an additional co-agent.

31. The process of claim 30, wherein the additional co-agent is a polymer.

32. The process of claim 31, wherein the polymer is an alkylated polyvinylpyrrolidone.

33. The process of claim 26, further comprising the step

of drying the composition.

34. A process for rheologically modifying a water-immiscible liquid comprising the steps of:

- (1) mixing hydrophilic insoluble cellulose with a co-agent to form a composition; and
- (2) mixing said composition in the water-immiscible liquid;

wherein said co-agent is capable of forming hydrogen bonds with said hydrophilic insoluble cellulose and is soluble in the water-immiscible liquid.

35. The process of claim 34, wherein mixing is accomplished by high shear mixing.

36. The process of claim 34, wherein mixing is accomplished by a homogenization.

37. The process of claim 34, further comprising the step of mixing the cellulose and co-agent together in a water-miscible solvent before mixing again in the water-immiscible liquid.

38. The process of claim 37, wherein the co-agent is a surfactant.

39. The process of claim 38, wherein the surfactant is selected from the group consisting of long-chain fatty acids, mono- and di- glyceride, alkylamines, and long chain alcohols.

40. The process of claim 38, further comprising the step of adding an additional co-agent.

41. The process of claim 40, wherein the additional co-agent is a polymer.

42. The process of claim 41, wherein the polymer is an alkylated polyvinylpyrrolidone.

43. The process of claim 42, wherein the polymer is added directly to the water-immiscible liquid.

44. The water-immiscible liquid of claim 21, wherein said water-immiscible liquid is capable of maintaining viscosity for at least 1½ years.

45. The water-immiscible liquid of claim 21, wherein said water-immiscible liquid has an increase in yield stress.

46. A drilling fluid comprising the composition of claim 1.

47. A paint solvent comprising the composition of claim 1.

48. An epoxy system comprising the composition of claim 1.

49. An industrial lubricant or grease comprising the composition of claim 1.

50. A thin film or powder coating comprising the composition of claim 1.

51. A vegetable oil comprising the composition of claim

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